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Electrically induced strain and polarization fatigue in lead-free ceramics

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Electrically induced strain and polarization fatigue in lead-free ceramics

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TABLE OF CONTENTS

ABSTRACT

Piezoelectric ceramics have traditionally been used in commercial applications such as actuators and sensors. By far the most popular piezoceramics currently in use are $Pb(Zr,Ti)O_3$-based (PZT) ceramics. PZT ceramics are able to produce large strain and polarization with the application of an electric field, and this is due to the Morphotropic phase boundary (MPB). A MPB is associated with the boundary between tetragonal and rhombohedral perovskite phases. A disadvantage of PZT ceramics is that they contain ≥ 60 wt. % of lead. Since lead is toxic, this poses an environmental and health hazard because lead is released into the surroundings during fabrication and disposal. Because of this, there is a push to discover lead-free alternatives that have comparable properties to PZT but none of the health risks. One possibility is $Bi_{1/2}(Na_{0.8}K_{0.2})_{1/2}Ti_{0.985}Ta_{0.015}O_3$ (BNKT-1.5Ta). In addition to comparable electrical properties, any lead-free alternatives must have decent fatigue resistance to be useful for applications.

This thesis focuses on the fatigue properties of BNKT-1.5Ta. The composition demonstrates high strain for a given applied electric field. To determine the fatigue resistance of BNKT-1.5Ta, data was gathered on how strain and polarization changed over number of cycles. Furthermore, fatigue tests at different temperatures were performed to ascertain if temperature affected fatigue life. X-ray diffraction (XRD) patterns and dielectric measurements were also collected to further examine any change in crystal structure and relative permittivity, respectively, before and after cycling.

CHAPTER 1: INTRODUCTION

1.1 Thesis Organization

This thesis first states the motivation for the study of fatigue properties in lead-free ceramics. The section goes into detail about the current use of lead-based ceramics and the recent interest in lead-free alternatives.

Chapter 2 consists of a literature review of topics pertaining to the research. This includes but is not limited to: basic background information about ceramics, their uses, and their applications. In addition, the concepts of piezoelectricity, strain, polarization, and fatigue are clearly explained to prepare the reader for the research presented in this thesis.

In chapter 3, experimental procedures are described and data is presented measuring and cataloging the electrically induced fatigue properties of a lead-free piezoelectric ceramic. This includes the effect of temperature on fatigue properties and how cycling affects dielectric measurements.

The last chapter draws conclusions based on the research presented in this thesis. The paper concludes with prospects on future research, references, and acknowledgements.

1.2 Motivation

Today, piezoelectric materials are used as actuators and sensors in a vast array of applications such as energy harvesting, medical imaging, and minimally invasive surgery.[1,2,3] Piezoelectricity is the coupling between applied mechanical stress and electric displacement (direct effect) and applied electric field and mechanical strain (converse effect).[1,4] Because of this unique property, piezoelectric materials possess the ability to convert mechanical energy to electrical energy and vice versa.[1,5,6] Some of the best performing piezoelectric ceramics, also known as piezoceramics, are $Pb(Zr,Ti)O_3$-based ceramics—which will be referred to as PZT ceramics from now on—and are cheap to produce and are easy to process.[1] Compositions that demonstrate the best electromechanical properties tend to have a feature called the morphotropic phase boundary (MPB) which denotes where multiple phases coexist.[1] In PZT ceramics, the MPB is at the tetragonal-rhombohedral perovskite boundary. Despite showing strong piezoelectric properties, PZT ceramics pose health risks. Containing >60 wt. % lead, PZT ceramics release lead into the atmosphere during processing and they can potentially pollute ground water when they degrade.[5] Due to the health and environmental concerns of lead, many countries around the world are actively looking into lead-free piezoceramics to replace PZT ceramics.[7] During the race to find a lead-free piezoceramics, besides having comparable piezoelectric properties, the lead-free piezoceramics must have acceptable fatigue properties.

One of the greatest challenges ceramics undergo is fatigue. Defined as the failure of a material due to the cycling of forces, fatigue is one of the properties that most inhibits materials and especially ceramics from being used in applications. In the case of

applied mechanical forces such as stress, fatigue results in the initiation and growth of cracks, which lead to catastrophic failure.[8] Fatigue also affects functional materials, which are driven by electric or magnetic field and temperature. For example, repeated electric field cycling in ferroelectric and piezoelectric ceramics will induce electric fatigue, which manifests as reducing maximum strain and switchable polarization with increasing number of cycles.[8] This is a problem for applications that require consistent results over a large number of cycles such as actuators.[8] However, electrical properties can be mostly recovered by thermal annealing at a temperature above the Curie temperature assuming the sample has not suffered from mechanical fatigue.[8] In the case of piezoelectric ceramics, an electric field-induced strain means the ceramic undergoes both electrical and mechanical fatigue, and mechanical fatigue means cracks will form. The cracks will most likely form along the grain boundaries and domain walls where the interfacial energy is the highest, and once the cracks form, there is no process to dispose of them. With the goals of high piezoelectric properties and long fatigue life, researchers have researched different lead-free compositions.

The desire to find lead-free piezoceramics to replace PZT piezoceramics is leading researchers to study three main groups of ceramics: alkali-niobium-based $(K,Na)NbO_3$ (KNN), bismuth-alkali-based $(Bi_{1/2}Na_{1/2})TiO_3$ (BNT), and barium-based $BaTiO_3$ (BT).[5,6] Despite strides made in the several past years, researchers are yet to find a material that has properties comparable to PZT. BT is relatively easy to process and manufacture but does not have a d_{33} value comparable to PZT. KNN systems have a wide working temperature range and high piezoelectric response, but they suffer from high porosity. Porosity is the concentration of pores in a sample. High porosity leads to

poorer properties and can only be avoided through special fabrication processes. BNT systems produce dense samples using the conventional solid solution reaction method but do not show as good properties as the KNN systems as by d_{33} values which represent the piezoelectricity of a material.[9] To enhance lead-free ceramics, two possible strategies are adding dopants and optimizing processing conditions. The goal of adding dopants is to slightly adjust the composition of a material in order to induce a MPB. The goal of optimizing processing conditions is to reduce porosity and increase the quality of individual samples. Given these methods to enhance lead-free piezoceramics, it would be possible to develop one system to overcome its shortcomings.

Research suggests that $(Bi_{1/2}Na_{1/2})TiO_3$-$BaTiO_3$ (BNT-BT) solid solutions have excellent piezoelectric properties and a large working temperature range, and this makes BNT-BT systems promising candidates to replace PZT systems.[5,10] Work by previous group members show that the BNT-BT system can be doped with increasing mol% of $BaTiO_3$ to change the crystal structure at unpoled, ambient conditions from monoclinic Cc, to rhombohedral R3c, to tetragonal P4bm, to tetragonal P4mm.[11] Additionally, increasing temperatures induce phase transitions from ferroelectric, to relaxor anti-ferroelectric, to normal anti-ferroelectric, to paraelectric.[11] A physical representation of these phenomenon are presented in Figure 1. The P4bm phase has nanometer-sized polar domains and demonstrate relaxor behavior, and this allows it to be poled with a d_{33} of 165 pC/N.[12] Despite this good piezoelectric behavior, there is a better alternative.

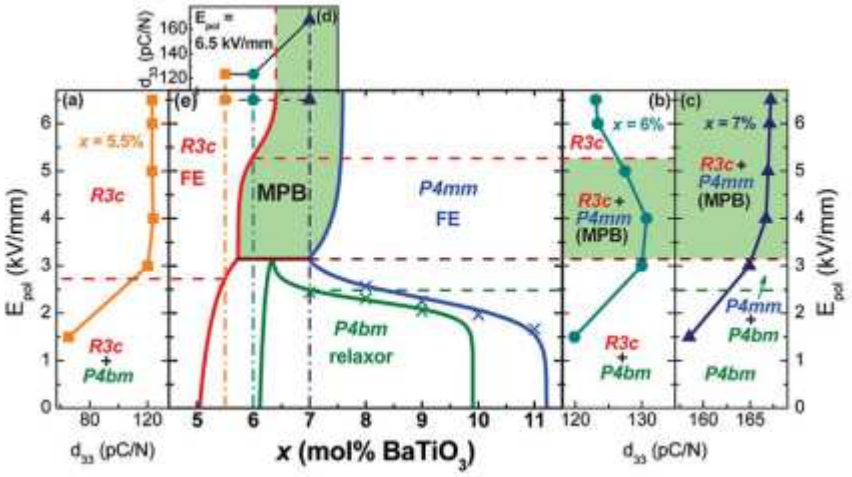


Figure 1: Poling field vs composition *x* phase diagram for (1-x)$(Bi_{1/2}Na_{1/2})TiO_3$-x$BaTiO_3$ solid solution. Determined using in-situ TEM analysis.[11]

Another possible system to replace PZT is a $(Bi_{1/2}Na_{1/2})TiO_3$-$(Bi_{1/2}K_{1/2})TiO_3$ (BNT-BKT) solid solution. When comparing d_{33} values, BNT-BKT systems perform better than BNT-BT, and because of this, there has been an increase of interest in developing and modifying BNT-BKT systems to have both high d_{33} and electrostrain values.[13] The incorporation of small amounts of dopants have recorded positive effects on the properties of BNT-BKT systems. The introduction of Sr reduces the depolarization temperature T_d while the dopant Nb suppresses the formation of oxygen vacancies and transform the ceramic into a pseudo cubic relaxor phase because of the reduction in lattice distortion.[14,15] These two dopants increase piezoelectricity, which causes high electrostrain, but requires extremely precise manufacturing conditions. As such, Ta is used as a dopant instead of Nb and Sr to modify the BNT-BKT system. Using Ta as a dopant both reduces T_d and increases electrostrain while being easier to process than a system that requires both Nb and Sr dopants.[16] The mol % of Ta added

considerably affects the properties and there is a maximum in electrostrain with 1.5% Ta doping as seen in Figure 1-2.[17]

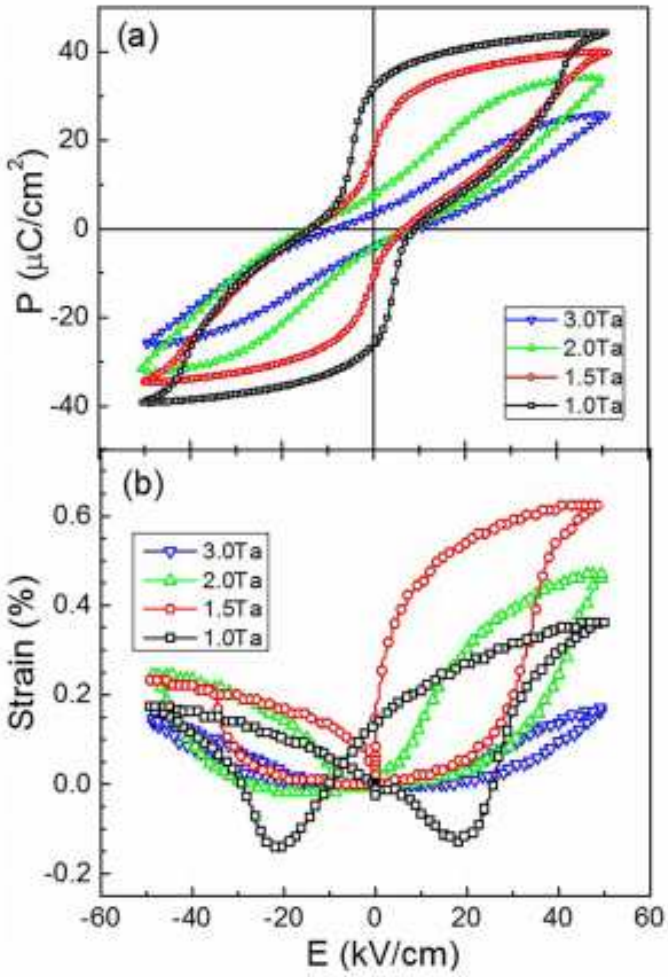


Figure 1-2: $Bi_{1/2}(Na_{0.8}K_{0.2})_{1/2}Ti_{1-x}Ta_xO_3$ (BNKT-xTa) strain and polarization as a function of mol % Ta doping[17]

Additionally, BNKT-1.5Ta demonstrates the electrocaloric effect.[18] The fatigue properties of the BNKT-1.5Ta system is presented in this thesis.

CHAPTER 2: LITERATURE REVIEW

The research thesis focuses on the testing and cataloguing of the fatigue of electrical properties of BNT-1.5Ta. This chapter consists of fundamental terms and concepts such as piezoelectricity, ferroelectricity, perovskite structure, etc. The applications of these materials are listed and explained.

2.1 Ceramics

Originally used to describe clay-based products and materials, the term "ceramic" is derived from the Greek word "keramos" for pottery. In modern vernacular, ceramic is used to describe any polycrystalline, nonmetallic, inorganic material. Amorphous materials with no crystal structure and single crystal materials can technically be defined as ceramics. For the sake of this thesis, ceramics will be defined as polycrystalline, inorganic, nonmetallic material that is not defined as a glass, polymer, or fall under another material category.[19] Despite the nuances on the definition of a ceramic, most ceramics share similar properties.

Ceramics are traditionally brittle, thermally and electrically insulating, and otherwise stable. Yet, ceramic science has challenged the notion of what ceramics are capable of, and what a ceramic is. For example, zirconium oxide, or zirconia, doped with small amounts of yttrium oxide make for a tough ceramic. Instead of breaking once reaching a critical force limit, zirconia can repeatedly survive high stress situations that makes it applicable for scissors, knives, and grinding balls used for milling. There are also electrically conducting ceramics used as transparent conductive coatings in modern

displays and thermally conductive diamond. Another class of ceramics are the piezoceramics, which demonstrate piezoelectricity.

2.2 Piezoelectricity and Ferroelectricity

For the purposes of this thesis, the material properties of piezoelectricity and ferroelectricity must be understood. Piezoelectricity is a useful and unusual material property. Normally, the mechanical and electrical properties of a material are separate from each other; in other words, they are independent of one another. However, piezoelectricity is the property of having intertwined or dependent electrical and mechanical properties.[1] The more "piezoelectric" a material, the more interconnected its mechanical and electrical properties. One way to understand the piezoelectricity of a material is through the relationship of its mechanical strain (S) and electric polarization (P).[1]

$$P = d\sigma \qquad (2\text{-}1)$$

$$S = dE \qquad (2\text{-}2)$$

Equations 2-1 and 2-2 represent the direct and converse piezoelectric effect, respectively. σ is applied stress and E is applied field. Represented in units of (C/N) or (m/V), d is the piezoelectric coefficient and is a representation of the piezoelectric behavior of a material; the larger the value, the more piezoelectric the behavior. Usually, d is represented as a third rank tensor (d_{ijk}) since strain is a second rank tensor and electric field is a first rank tensor. However, for the research presented in chapter 3, it is assumed that all strain and polarization takes place along the same direction as the

applied electric field and stress, respectively. For large-signal i.e. large electric field or stress applications, d_{33} is the piezoelectric constant and is a function of the applied field or stress. Up until now, piezoelectricity has been defined for a single crystal, but for polycrystalline ceramics, other factors must be taken into consideration.

Typically, polycrystalline ceramics do not have macroscopic polarization due to their randomly oriented grains. When an electric field or stress is applied, all the grains will produce strain or polarization, respectively, in their randomly oriented directions, and this will result in a negligible to net-zero result. This phenomenon makes polycrystalline materials isotropic. As such, for piezoelectricity in polycrystalline ceramics to be possible, the grains must seemingly be able to align. Piezoelectricity in polycrystalline ceramics is possible due to a property called ferroelectricity. A ferroelectric material is one that has spontaneous polarization and the direction of the polarization can be re-oriented with an applied electric field.[1] Ferroelectricity is possible due to the presence of ferroelectric domains: volumes of uniform polarization inside a ceramic. It is these domains that can be reoriented with an applied electric field.

Since ferroelectric materials have re-orientable domains, they tend to form dipoles and can be characterized as polar materials. One way to discover whether a material is polar is through a property called pyroelectricity. In short, pyroelectricity is the property of a material to generate an electric charge under uniform heating or cooling.[1] Only polar materials demonstrate pyroelectricity since a change in magnitude of dipoles is needed to produce a net dipole and net polarization upon thermal expansion or contraction. Yet, the net polarization will be neutralized once charges collect on the surface.[20] It should be noted that piezoelectric materials do not necessarily need to be pyroelectric as they can be

heated non-uniformly to produce a charge and a stress. Therefore, ferroelectricity enables polycrystalline ceramics to under piezoelectricity. The factor that determines whether a polycrystalline ceramic is ferroelectric is the crystal structure of its unit cells.

2.2.1 Crystal Symmetry

Ordinarily in crystallography, crystals can be categorized into one of 32 general point groups. A point group is a specific set of symmetry operations (rotation, inversion, reflection, etc.) in regards to the structure of the unit cell. If one takes the possibility of magnetism into consideration, there are 122 possible point groups, and that does not consider unorthodox cases such as quasi-crystals. Since the subject of the research in this thesis follows a non-magnetic piezoceramic, the only the original 32 points groups will be considered to determine which point groups, i.e. crystal structures, allow for ferroelectricity and piezoelectricity.

For a ceramic to be ferroelectric and piezoelectric, the point group must be non-centrosymmetric. Centrosymmetry is the property that a crystal structure has no dipole in its relaxed state. An applied electric field can cause the cation to shift one direction and the anions to shift the opposite direction which will induce a dipole, but the centrosymmetric crystal structure will revert to its original structure when the electric field is dispelled. On the other hand, non-centrosymmetric point groups are necessary for piezoelectricity since they have an inherent dipole built into their structure, which allows polarization to be induced using stress. Examples of centrosymmetric and non-centrosymmetric structures cans be seen in Figure 2-1.

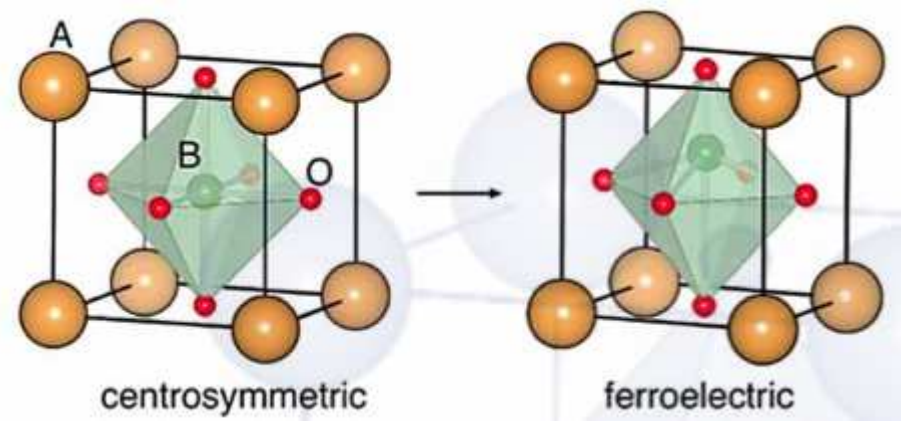


Figure 2-1: Examples of centrosymmetric and non-centrosymmetric structures. The non-centrosymmetric structure is assumed to be ferroelectric in this example[21]

Out of 32 point groups, 21 are non-centrosymmetric, and of those 21, only 20 point groups support piezoelectricity. In these 20 point groups, applying normal or shear stress will induce polarization in the crystal structure. Though the requirement for piezoelectricity is fulfilled, ferroelectricity is not yet guaranteed.

For ferroelectricity to occur, there must be a dipole oriented along an axis. This dipole, which did not need applied stress nor electric field, is the reason for spontaneous polarization. Out of the 20 piezoelectric point groups, 10 "polar" point groups fulfill this requirement. Another requirement for ferroelectricity is that these dipoles must be re-orientable which leads to re-orientable, spontaneous polarization. Physically, this means that when polarization is in one direction, the coercive field, the electric field required to reverse the polarization, must be lower than the dielectric breakdown of the material. There are only a handful of the 10 polar groups that also meet this requirement. Figure 2-2 summarizes which point groups can display which property.

To summarize, polycrystalline ceramics will have randomly oriented grains. The random orientation will give the polycrystalline ceramic a spherical symmetry, which is centrosymmetric. Normally, polycrystalline ceramics are isotropic, but the application of an electric field can align the domains. This induces a net dipole and net polarization in the polycrystalline ceramic and it can now display piezoelectricity like its single crystal counterpart. The net polarization is a result of conical symmetry of the polycrystalline ceramic. The specifics of the shift from the spherical to conical symmetry is studied through a well-known structure.

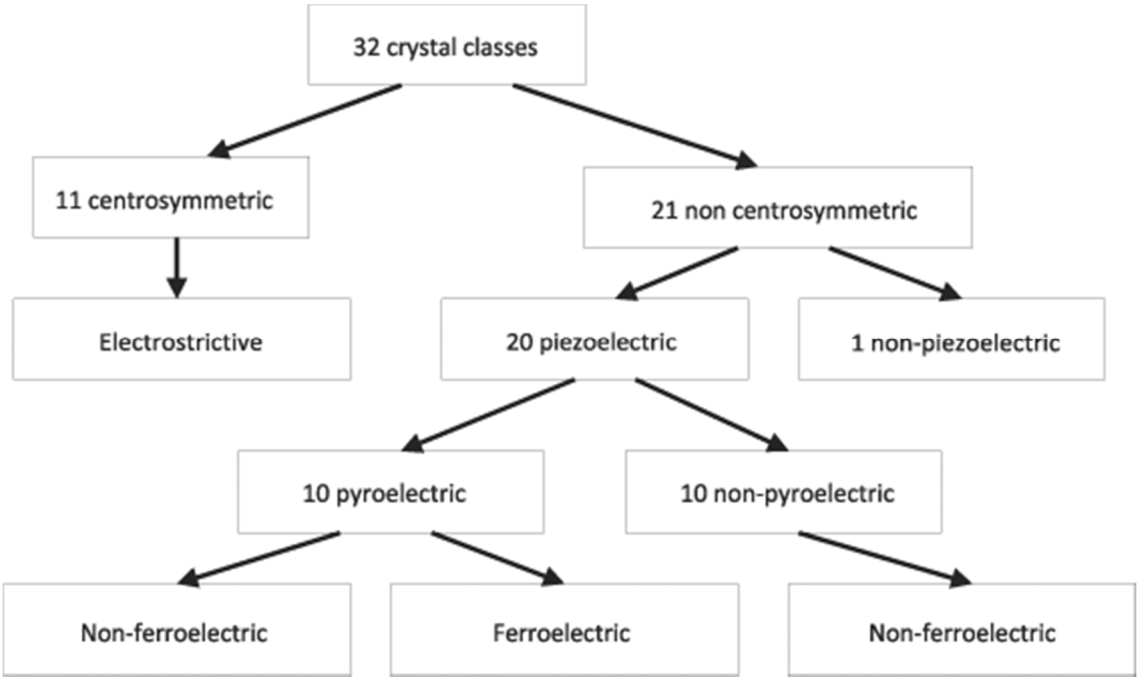


Figure 2-2: Diagram summarizing which point groups fall into each category of electronic properties.[22]

2.3 Perovskite Structure

One of the most applicable and simplest crystal structures that has the potential to allow for ferroelectricity is the perovskite structure. Named after the $CaTiO_3$ mineral, the perovskite structure ideally possesses cubic, centrosymmetric m 3bar m symmetry as shown in Figure 2-3.

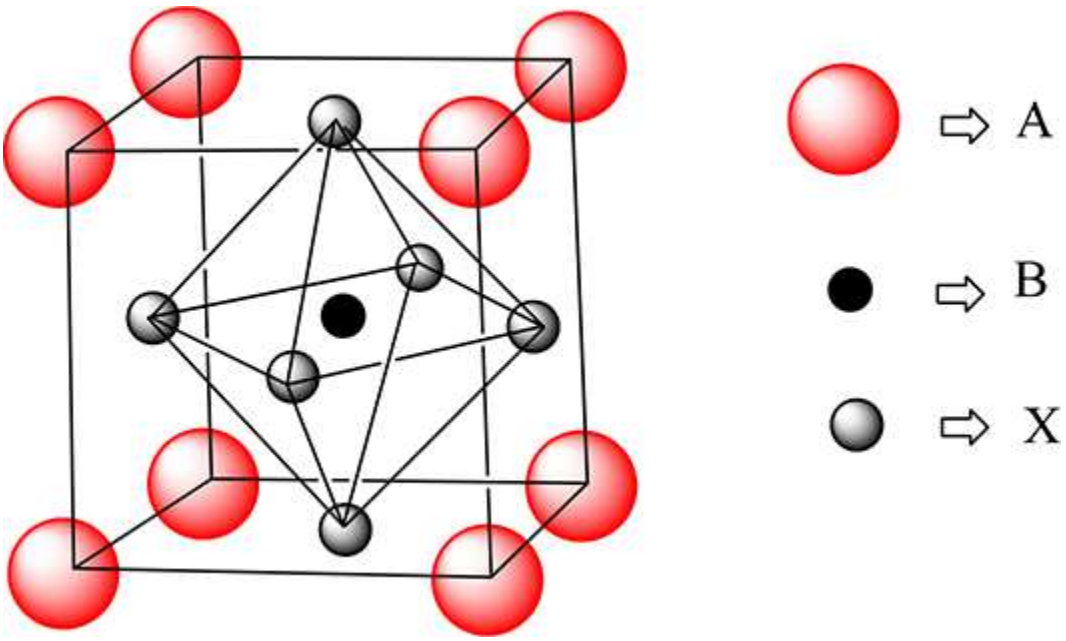


Figure 2-3: Ideal perovskite structure unit cell[23]

The basic ABX_3 structure allow for a wide range of ions to inhabit the perovskite structure. Since the research presented in this thesis deals with an ionic perovskite structure, it can be assumed that the X-site is an anion with a charge of -2. Specifically for lead-free piezoceramics, the X-site anion is assumed to be oxygen. Likewise, the A and B-sites would be inhabited by cations with a combined charge of +6. Multiple combination of A and B charges are possible such as +1/+5 and +3/+3, but +2/+4 is the most common. Since the B-site cation is in the center of the unit cell and the X-site

anions are on the walls, the B-site cation with the six adjacent X-site anions can be interpreted as an octahedra. In addition, there can be a wide range of A, B, and X-site ion sizes.

There are multiple elements with varying ionic sizes that can fill the different sites. The only limitation is that ions cannot physically overlap each other. In the theoretical case with the maximum amount of volume filled in the unit cell, the A and X ions would be touching and the B and X ions would also be touching. Assuming that *s* is the length of the side of the cubic unit cell, two equations determine the allowable sizes of the ions:

$$s\sqrt{2} = 2r_A + 2r_X \qquad (2\text{-}1)$$

$$s = 2r_B + 2r_X \qquad (2\text{-}2)$$

From these equations, it can be deduced that the B cation will be smaller than the A cations. A ratio of the two equations can be formed such that:

$$\sqrt{2} = \frac{r_A + r_X}{r_B + r_X} \qquad (2\text{-}3)$$

Dividing both sides by √2, the ratio becomes:

$$1 = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \qquad (2\text{-}4)$$

Assuming that there are non-ideal cases, the 1 is switch with the Goldschmidt tolerance factor *t* which gives the equation:

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \qquad (2\text{-}5)$$

The Goldschmidt tolerance factor *t* represents the stability and shape of the perovskite structure. It is a function of the ionic radii, and the ionic sizes, of the A, B, and X-site ions, and it assumes ionic bonding. With $t = 1$ representing the ideal cubic structure, the perovskite structure is stable when $0.9 < t < 1.1$. Any *t* values outside of this range is not possible because the perovskite structure would be deformed beyond a critical threshold as to not be feasible. Therefore, the perovskite structure can be non-centrosymmetric and demonstrate ferroelectricity if the A, B, and X sites are filled with elements that fulfill the charge requirement but do not have ideal ionic sizes. Other factors such as defects, solid solution characteristics, and covalent bonding may cause the perovskite structure to further deviate from the Goldschmidt tolerance rule. This translates as distortions in the perovskite structure.

2.3.1 Distortions

There are five types of distortion directions when the perovskite structure is "pulled or squeezed" : <001> tetragonal, <110> orthorhombic, <111> rhombohedral, arbitrary <hk0> monoclinic, and arbitrary <hkl> triclinic. The number of possible polarization states depends on the distortion direction. In a cubic perovskite structure, piezoelectricity is impossible because of the centrosymmetry. Distortions can make an A-site ion, B-site ion, or both unstable in their corner or center positions, respectively, and this allows the unstable ion(s) to shift from its ideal position to a position that will allow for spontaneous polarization. Application of an electric field or stress will demonstrate ferroelectricity and piezoelectricity, respectively. The instability of the cations is the primary cause of spontaneous polarization, and other distortions such as tilting and rotation of the BX_6 octahedra can add to the spontaneous polarization.[24]

2.4 Domains and Polarization

For a ferroelectric material, each unit cell possesses its own dipole and its own polarization. When a group of adjacent unit cells has aligned dipoles, the sum of their polarizations add up to form a net polarization.[5,7] This group of aligned unit cells is called a ferroelectric domain. Domains occur in both single crystals and polycrystalline ceramics. In polycrystalline ceramics, domains tend to form in grains as opposed to across grains. It is possible for different domains to exist within the same crystal or same grain because each domain is caused by different distortions. Theoretically, in a single crystal, if the perovskite structure underwent only one distortion with no other defects, there would be one grain in the crystal. Realistically, the there are multiple types of distortions each with its own direction and magnitude even in a single crystal. The boundary between two unlike domains is called the domain wall. The domain wall reduces electrostatic and elastic distortion energy.[25,26]

Spontaneous polarization in ferroelectric materials is due to the net polarization of the domains oriented in polarization direction. It is still possible for other domains in different directions to exist given that the conditions of the ceramic permits it (i.e. antiferroelectric ceramics). Therefore, the orientation of any other domains will depend on the crystal structure of the ceramic.[25] For example in a tetragonal structure with <100> distortions, there are six possible distortion directions, and that means domains are parallel, perpendicular (90°), or anti-parallel (180°). Any adjacent domains that are not parallel nor anti-parallel with each other will produce a strain across their domain wall.

A ceramic develops domains during the cooling from the paraelectric to ferroelectric or relaxor ferroelectric phase; the first time this happens is during the end of sintering when the ceramic is being cooled down to room temperature. Idealistically, the ceramic sample would cool uniformly and form one domain, but non-uniform cooling and other defects such as pores lead to stresses being produced during the phase transition. These stresses vary in direction and magnitude and cause different domains to form. When a stress is applied (or alternatively electric field for piezoceramics) in a certain direction, all non-parallel domains exhibit spontaneous strain. This property is called ferroelasticity and it is important factor when designing materials that have mechanically dependent electrical properties.[27] It is possible to change the direction of domains without annealing the sample.

If a large enough electric field is applied to a ferroelectric ceramic, the domains parallel to the electric field direction grow until they can overtake adjacent domains. When this happens, the adjacent domains effectively had their dipoles forcefully oriented with the electric field direction. This essentially combines domains together and increases the net polarization of the ceramic. This process is called domain growth. Since domain growth is induced by applied electric field and net polarization is affected by domain growth, domain growth can be visually represented by a polarization vs electric field hysteresis loop. This is shown in Figure 2-4.

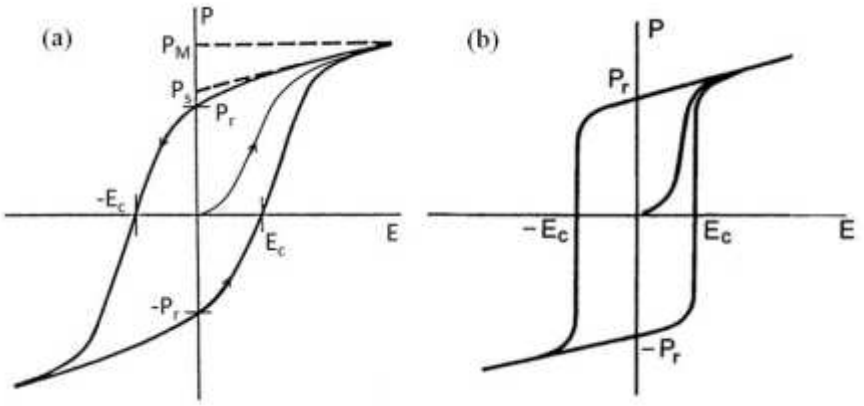


Figure 2-4: Sample ferroelectric a) round and b) square polarization vs electric field hysteresis[1,28]

Compared to ferroelectric ceramics, dielectric materials have a linear relationship with applied electric field. The initial application of the electric field begins the process of the gradual domain growth. During the poling process, the polarization demonstrates linear dependence on applied electric field as the domains closest aligned with the electric field grow to inhabit whole grains. The polarization when the maximum electric field is applied is called maximum polarization P_M. The polarization still present after the electric field has been released is called the remanent polarization P_R which is typically smaller than spontaneous polarization P_S (described as the linear projection of maximum polarization at zero electric field). The difference between spontaneous and remanent polarization is a reflection of the percent volume of the ceramic that remains poled after the electric field is released. The electric field required to randomize all domains and counteract the remanent polarization is called the coercive field E_C, and this is where domain reversal occurs. Remanent polarization and coercive field are the most important values when talking about ferroelectrics since they represent how much energy will be required to pole a sample in a given direction.

A gradual unpoling of domains leads to a "round" hysteresis loop while a sudden unpoling of domains leads to a "square" hysteresis loop; this can be seen in Figure 2-4 (a) and (b), respectively. The hysteresis shape is primarily influenced by domain structure, but the rate of change in electric field may also affect the shape.[1] Despite perovskites showing ferroelectric behavior, their domains show more complex behavior.

2.5 Structural Phase Transitions

Phase transitions may occur due to temperature, pressure, or electric field. For the sake of simplicity, only the effects of temperature will be most discussed. At high temperatures, perovskite ceramics favor a cubic phase, and as temperature decreases, may undergo one or multiple phase transitions. Since a phase transition usually involves a change in crystal structure, distortions form in the perovskite structure because of imperfect ion sizes or other imperfections such as covalent bonding. The structural phase transitions can be first order, second order, or a combination of the two.

First order transitions involve an instantaneous jump from one phase to another. The Clausius-Capeyron equation relates the slopes of the thermodynamic potential curve of phase equilibrium (A-B in Figure 2-5) with respect to temperature and pressure to the changes in volume Δv and entropy ΔS that occur during a first order transition.[28]

$$\frac{dT}{dp} = \frac{\Delta v}{\Delta S} \qquad (2\text{-}6)$$

In a first order transition, the required thermodynamic driving force results in a thermal hysteresis where the heating and cooling curves will have different transitions

temperatures. This is represented in Figure 2-5 where the heating curve 5-4-6-2-1 displays overheating with a higher transition temperature while the cooling curve 1-2-3-4-5 displays undercooling with a lower transition temperature. First order transitions manifest themselves as sudden changes of properties between two phases and register as exothermic or endothermic peaks in calorimetric measurements.

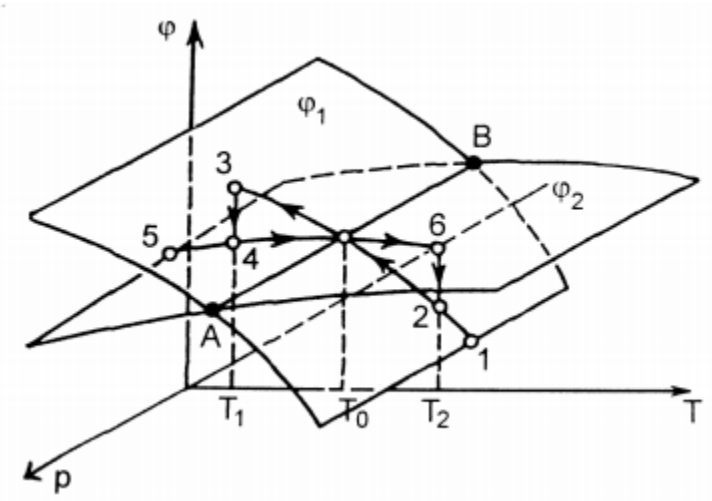


Figure 2-5: First order transitions between two thermodynamic potential surfaces of two different crystal structures[28]

Dielectric measurements measure the dielectric constant of a material against temperature. For perovskite ceramics, the Curie-Weiss law can model the dielectric measurements where C is the Curie constant, T_0 is the Curie temperature, and the Curie point T_C is the actual transition temperature.

$$\epsilon_r = \frac{C}{T - T_0} \qquad (2\text{-}7)$$

The Curie point is the limit for ferroelectricity, and above the Curie point, the ceramic will most likely be in a paraelectric phase. As a high symmetry phase (paraelectric)

approaches the transition to a lower symmetry phase (ferroelectric) as temperature decreases, the dielectric constant increases. Theoretically, the permittivity would form a positive-infinite asymptote as the temperature approached the Curie temperature, but the permittivity drops dramatically once the temperature goes below the Curie point. In general, some second order transitioning precedes a first order transition.[28]

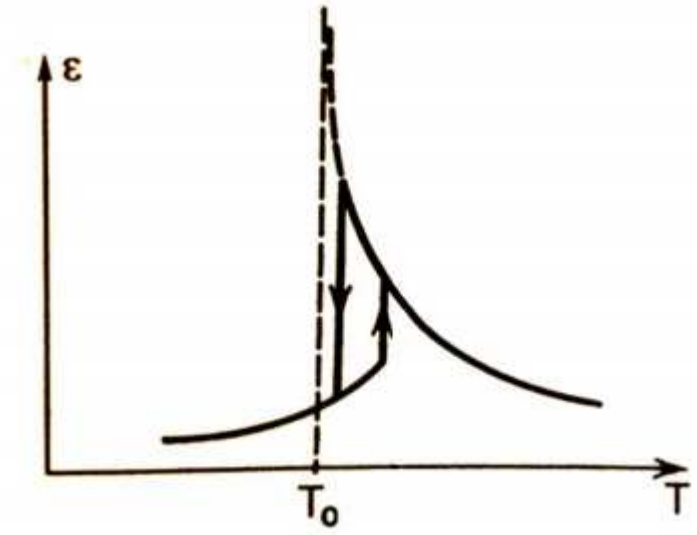


Figure 2-6: Example of Curie-Weiss law. Dielectric permittivity vs temperature for a first order transition[1]

Second order transitions occur over a wide temperature range and display gradual changes in structure compared to first order transitions. The diffusive transitions usually occur between similar phases; the lower symmetry phase does not contain any symmetry elements not present in the higher symmetry phase.[28] Characteristics of diffusive second order transitions include gradual changes in properties, large frequency dependence of dielectric properties (dielectric dispersion) across the transition, and lack of exothermic or endothermic peaks in calorimetric measurements. An example of second order transition can be seen in Figure 2-7.

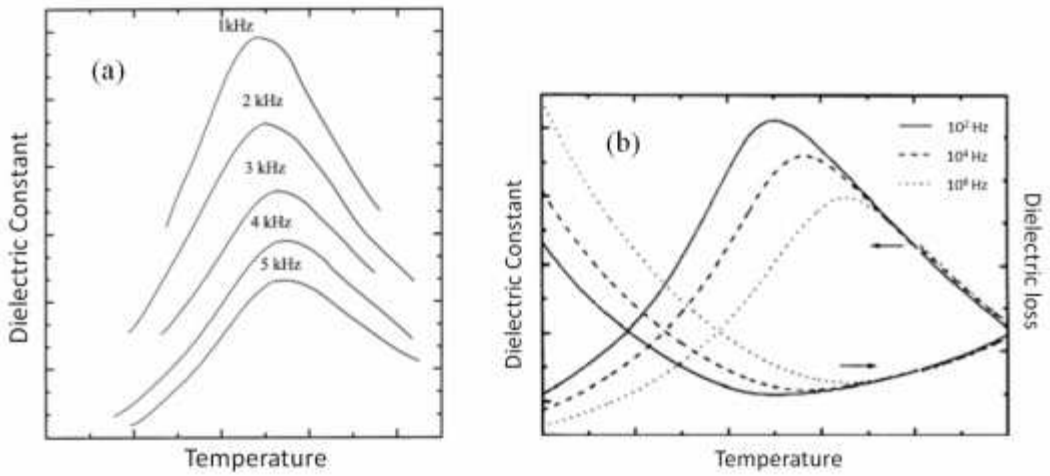


Figure 2-7: Examples of dielectric measurements of (a) second order diffuse transition[29] and (b) relaxor ferroelectric across T_m[30]

2.6 Relaxor Behavior

Since the perovskite structure has a tolerance range, many combinations of elements are possible, and this leads to many variations and combinations of distortions. In fact, sometimes a combination of distortions is so complex the ferroelectric domains in a ceramic can no longer display long-range order. Instead of micron-sized domains, the ceramic will have nano-sized domains (~5 nm) called polar nanoregions, and under this condition, the ceramic is characterized as relaxor ferroelectric. In addition, relaxor ferroelectric ceramics, or relaxors for short, can be divided into ergodic and non-ergodic groups.

Normally when measuring polarization, relaxors will produce a slim-loop hysteresis as seen in Figure 2-8.[31] This indicates that domain growth is not stable

because when the electric field is dissipated, the domains will tend to randomly orient themselves resulting in little to no remanent polarization. The difference between ergodic and non-ergodic relaxors is their behavior after being poled. Ergodic relaxors will still demonstrate relaxor behavior after poling while non-ergodic relaxors will demonstrate ferroelectric behavior. There are also some difference in phase transitions between ferroelectric and relaxor ferroelectric materials.

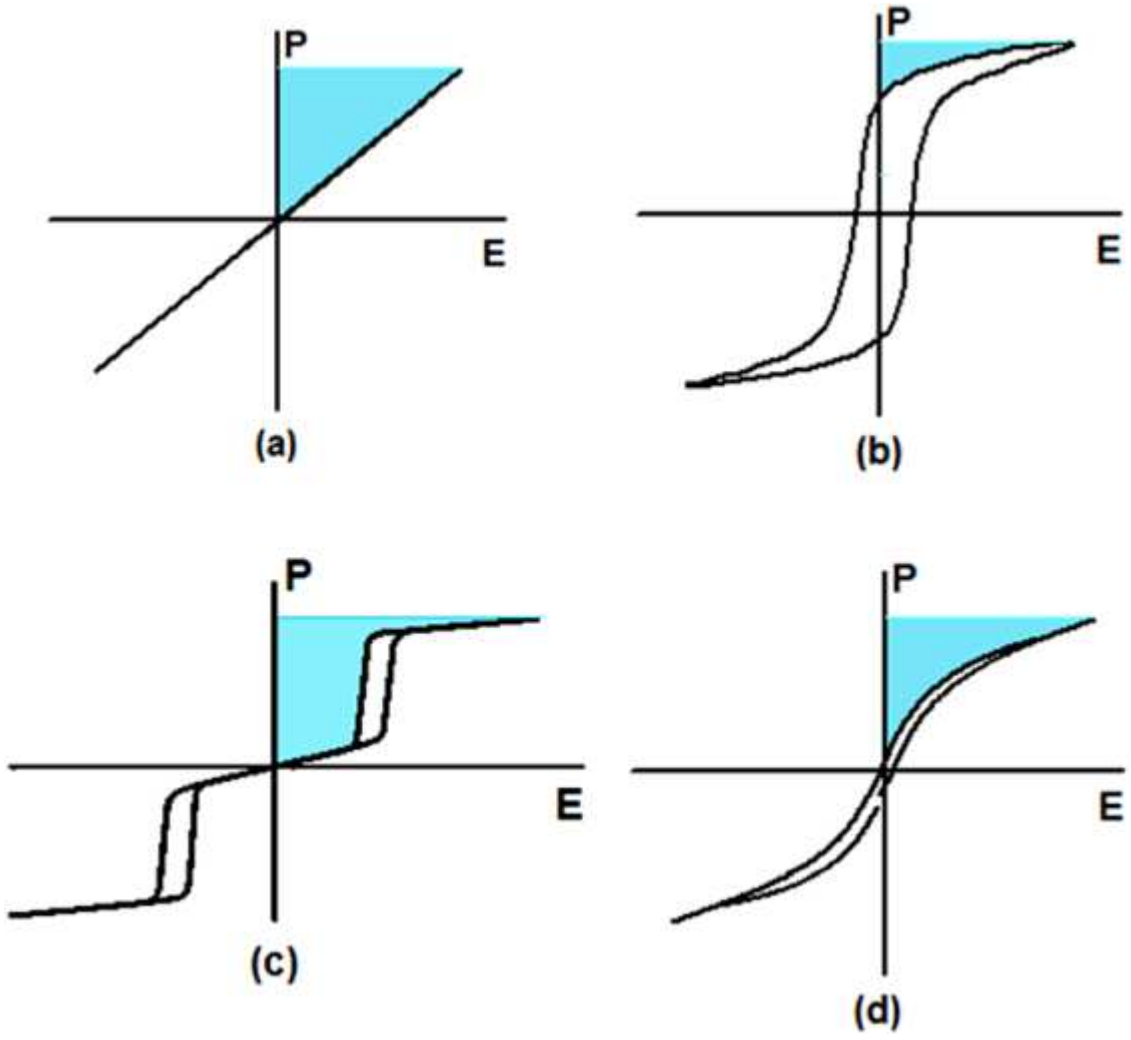


Figure 2-8: General behavior of polarization vs applied electric field hysteresis a) linear, b) ferroelectric, c) antiferroelectric, and d) relaxor ferroelectric materials.[32]

Different types of strain can be seen in Figure 2-9. Typically, strain is induced when adjacent domains are aligned neither parallel nor anti-parallel with each other. When an electric field is applied, this causes spontaneous strain to occur along the domain wall. In BNKT-1.5Ta specifically, the electric-field induced phase transition from rhombohedral R3c phase to the tetragonal P4bm phase also adds to the electrostrain.[17]

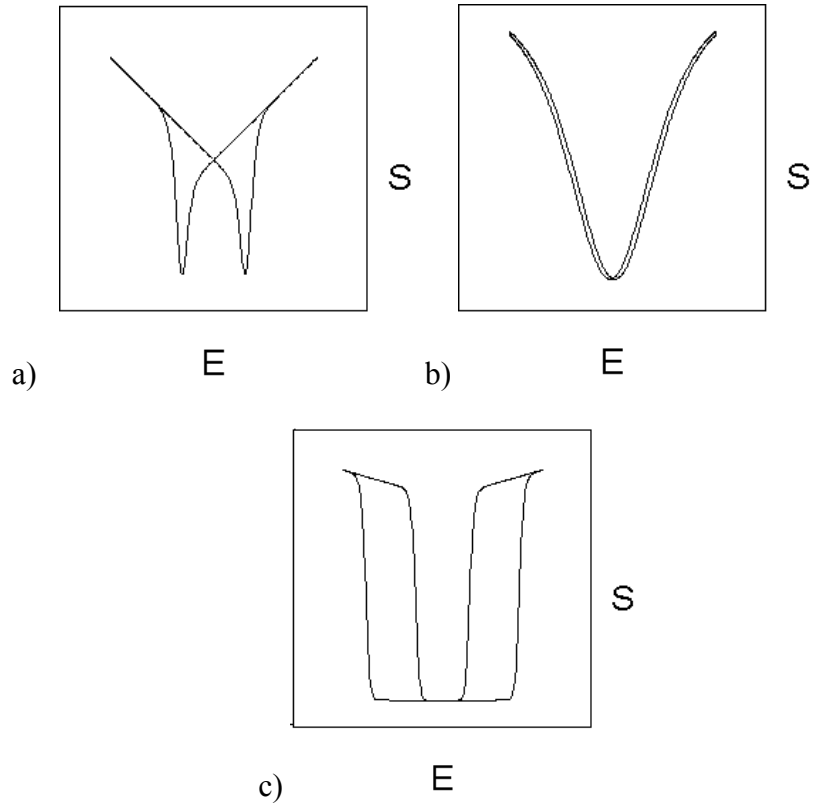


Figure 2-9: strain examples of a) ferroelectric, b) relaxor, and c) antiferroelectric behavior[33]

Normally in a ferroelectric material, the ferroelectric phase is at low temperatures and the paraelectric phase is at high temperatures. Like ferroelectrics, relaxor materials also have a high-temperature paraelectric phase, but as the material cools down, there is a phase transition into the ergodic relaxor phase where the nanoregions form. This is

neither a first order nor second order transition because there is no symmetry change during the transition. The temperature where this transition occurs is called the Burns Temperature T_B.[34] Relaxors do not follow the Curie-Weiss law because the ceramic can possess remnant polarization in relaxor phase instead of only the ferroelectric phase. Instead, relaxors have a peak in dielectric constant at temperature T_m. It should be noted that T_m is frequency-dependent since the nanoregions have time-dependent growth under applied electric field.[19] The change in domain morphology is the cause of the change of properties between phases, and this manifests as dielectric frequency dispersion. The relaxor can undergo a second transition at a lower temperature called the freezing temperature T_f.[34] A possible transition is from ergodic relaxor to non-ergodic relaxor where the nanoregions have fixed orientation, but it is also possible to have an ergodic relaxor to ferroelectric transition.

2.7 Applications

Because of their impressive electromechanical properties, piezoelectric ceramics have been used in commercial applications such as actuators and sensors. With an increasing need for functional materials and desire to eliminate the dependence on lead-based materials, there has been a huge spur of research on lead-free ceramics.[5] After decades of the material investigation into lead-free ceramics, there is a growing demand to transfer scientific knowledge into application.[6]

It should be noted that polycrystalline materials are more broadly used than single-crystal materials for a variety of reasons. Polycrystalline materials are easier and cheaper to make than single-crystal counterparts, demonstrate better mechanical

properties, and are more environmentally durable.[20] For this reason, polycrystalline ceramics are better studied, better understood, and more readily used for applications.

One such application is for electronics. As electronic devices become smaller and more powerful, they need to incorporate increasingly highly functional materials. Some advantages that make piezoceramics candidates for electronics is that they have predictable temperature and frequency behavior, high-temperature stability, high dielectric permittivity, and low dielectric loss compared to metals and semiconductors. Piezoceramics would be best suited as capacitors since they are naturally non-conductive. Specifically for lead-free piezoceramics, one problem they face is a phase transition around room temperature; this will change the properties of the ceramic and could seriously affect the performance of the electronic if it happens to be in a warm or cold environment. However, the additions of dopants to the composition of lead-free piezoceramics can lower the phase transition below room temperature to a temperature where the electronic would not be normally used, and as a result, this broadens the working range for lead-free piezoceramics.[35,36]

Another possible application is for sensors. For some sensors, it is important to measure applied mechanical stress. Piezoceramics fill this need since charge is produced under applied stress. This can be measured as dielectric displacement or polarization and is an example of the direct piezoelectric effect. Another application is actuators.

2.7.1 Actuators

As stated earlier, piezoelectricity is the property that allows polarization to be induced by applied stress and strain to be induced by applied electric field. This property

is great for actuators, which need to produce a desired strain consistently with a given input. The strain of an actuator can be simplified as:

$$S = dE + ME^2 \qquad (2\text{-}8)$$

There are several assumptions made with this equation. It is assumed that the electric field is applied along one axis and the strain is induced only along the same axis. It is also assumed that strain in actuators are caused by piezoelectricity and electrostriction. In equation 2-8, constant *d* relates the strain produced by piezoelectricity and constant *M* relates the strain produced by electrostriction. Normally there would be higher order terms caused by factors such as geometric dimensions and defects, but for the sake of simplicity, an ideal case will be assumed.

Electrostriction is a property held by dielectrics that a strain will be induced by an applied electric field. The difference between electrostriction and piezoelectricity is that when the applied electric field is reversed, the strain is induced in the same direction in electrostriction, but the strain would be induced in the opposite direction in piezoelectricity. If a piezoceramics is being used for actuator applications, it is assumed that the material displays strong piezoelectric behavior, and it can be assumed that *d* is significantly greater than *M*. As such, the electrostriction can be ignored and the strain equation simplifies to[37]:

$$S = dE \qquad (2\text{-}9)$$

In this case, *d* now represents the small-signal coefficient for piezoelectricity.

2.8 Fatigue

Fatigue serves as one of the biggest topics of research in ferroelectric groups for the past several decades because of its technological importance.[8] Fatigue hinders the long-term operation, reliability, and application of ferroelectric materials in piezoelectric actuators and microelectronic memories. During the service life of piezoelectric devices, the piezoceramics are subjected to repeated applied electric fields and this causes the functional properties of the piezoceramics to deteriorate. Piezoelectric materials undergo two types of fatigue: electrical and mechanical.

A sign of electric fatigue is the reduction of switchable polarization during repeating electric field reversal.[8] In addition to electric fatigue, piezoceramics undergo mechanical fatigue. Mechanical fatigue occurs due to the repeated cycling of strain due to applied stress or electric field. Microscopically, this causes deformations to form in the material in the form of defects such as vacancies and dislocations. Macroscopically, this manifests as cracks in the material. A sign of mechanical fatigue is the reduction of strain during repeating electric field reversal or repeating applied stress. The mechanisms responsible for the electrical and mechanical fatigue has yet to be clearly identified.

There is no consensus yet due to the complex nature of the degradation process, but several theories have been proposed. Many experimental and theoretical studies have been performed on PZT-based compositions to determine the origin of electric fatigue in piezoelectric materials. This includes phenomenological scenarios and microscopic mechanisms such as electrode degradation, near-electrode passive layer formation, nucleation inhibition, domain wall pinning, and local phase decomposition. When it comes to lead-free piezoelectric ceramics, there is not nearly as much literature studying

fatigue properties. One theory suggests that phase transition may be an important factor in the fatigue properties of lead-free piezoceramics, and that current models for lead-based materials may not be practical to lead-free equivalents. Further investigation of the degradation process of lead-free piezoceramics process is needed.

CHAPTER 3: ANALYSIS OF FATIGUE PROPERTIES OF LEAD-FREE CERAMICS

3.1 Introduction

Piezoelectric materials have the useful property of producing strain under an applied electric field and vice-versa. Because of this, piezoceramics are used in many applications such as sensors, actuators, in medical imaging equipment, and other commercial devices.[38] One of the most effective and heavily-applied piezoelectric systems is the lead-containing system $Pb(Zr,Ti)O_3$ (PZT), but there are problems associated with the disposal of products containing PZT. Because of the lead present in PZT, there are concerns that disposal of PZT will decompose and the lead can potentially contaminate ground water or the surrounding area. Due to the health concerns surrounding PZT, there has been a directed effort in academia and industry to find a lead-free piezoceramic.[5] There have been some promising lead-free replacements.

Among the lead-free solid solutions reported in literature, $(Bi_{1/2}Na_{1/2})TiO_3$-based compositions show promise of developing high strain under applied electric field. Another more promising solid solution is modified $[Bi_{1/2}(Na_{1-x}K_x)_{1/2}]TiO_3$. A possible reason for the high strain might be due to the *P4bm* phase found in the $(Bi_{1/2}Na_{1/2})TiO_3$ composition. When an electric field is applied, the relaxor phase nanometer-sized domains will change into a ferroelectric phase with micron-sized domains.[11] The volume change associated with the reversible phase change is responsible for the high

longitudinal electrostrain.[5] In addition to basic electronic and mechanical properties, cycling effects must also be considered.

The stability of properties as a function of cyclic electric field loading is an important concern for device applications. The degradation behavior in lead-free piezoceramics seems to correlate with the presence of electric field induced phase transitions.[39,40] The evolution of electrostrain hysteresis under unipolar and bipolar cyclic field at different temperatures is explored in this thesis.

3.2 Experimental Procedure

Polycrystalline $Bi_{1/2}(Na_{0.8}K_{0.2})_{1/2}Ti_{0.985}Ta_{0.015}O_3$ (BNKT-1.5Ta) was fabricated using the solid-state reaction method. The raw materials of Na_2CO_3 (≥99.9 wt%), K_2CO_3 (≥99.0 wt%), Bi_2O_3 (≥99.9 wt%), TiO_2 (≥99.99 wt%), and Ta_2O_5 (≥99.99 wt%) were mixed in ethanol according to stoichiometry, stored in a bottle, and milled in a vibratory mill for seven hours. The resulting slurry was transferred to a drying dish, and after drying, the BNKT-1.5Ta mixture was pressed into a single pellet and calcined for 3 hours at 850°C in a Barnstead Thermolyne 47900 furnace. All steps before the calcination including the transfer of the slurry/powder were crucial because the slurry/powder was an unreacted mixture of powders; it would be easy to lose some powders, affect the stoichiometry, and change the resulting composition. The calcined powders were again mixed with ethanol, bottled, and milled for another seven hours. The slurry was transferred a second time to a drying dish and was properly dried. The resulting powder underwent uniaxial pressing into circular disks. Great care was needed to apply the

pressure evenly across the surface area of the pellet and to load and unload the pressure slowly as to not induce a crack in the green pellet. These pellets were sintered for 3 hours at 1150°C in a Carbolite RHF 1600 furnance. To prepare the pellets for testing, they were grinded down to a thickness between 0.50-0.65 mm. The grinded pellets were polished using sandpapers of increasing grit; finishing with a diamond paste. For electrical properties measurements, silver coating was sputtered on both sides of a polished ceramic using "masks" which would leave a ring of unsputtered area on the perimeter of the surfaces. An Edwards SCANCOAT 6 was used for the sputtering. The silver coating acted as the electrodes. In addition to preparing the pellets, lab equipment was used to apply electric field and record the resulting measurements. For polarization measurements, the polarization hysteresis (P-E) loops were recorded at 4 Hz using a standard ferroelectric test system RT-66A (Radiant Technologies, Albuquerque, NM, USA) with a peak field of 50 kV/cm. The strain was monitored using a MTI-2000 Fotonic Sensor (MTI Instruments Inc., Albany, NY, USA), a Tektronic DPO 2014B Digital Phosphor was used to record the raw data, an Agilent 3320A 20MHz Function/Arbitrary Waveform Generator was used to apply an electric field, and a TREX Model 10D H.V. Supply Amplifier/Controller was used to amplify the inputted field to have a desired peak of 50 kV/cm. The ceramic was placed in a custom-built sample holder that held a silicon oil bath, which prevented arcing for the duration of the experiments. To prepare the ceramic for low-temperature measurements, the ceramic and sample holder were placed inside the Delta Design- DELTA 9023 temperature chamber which was programmed to cool the chamber using liquid nitrogen from a tank supplied from ChemStores. For high-temperature measurements, the ceramic was placed in a

silicon bath on top of a Fisher Scientific ISOTEMP hot plate to heat the sample and an Omega HHM8229 Digital Multimeter was used to measure the ambient temperature of the silicon bath. Pictures of the equipment used for the strain measurements at different temperatures are shown in Figure 3-1.

a)

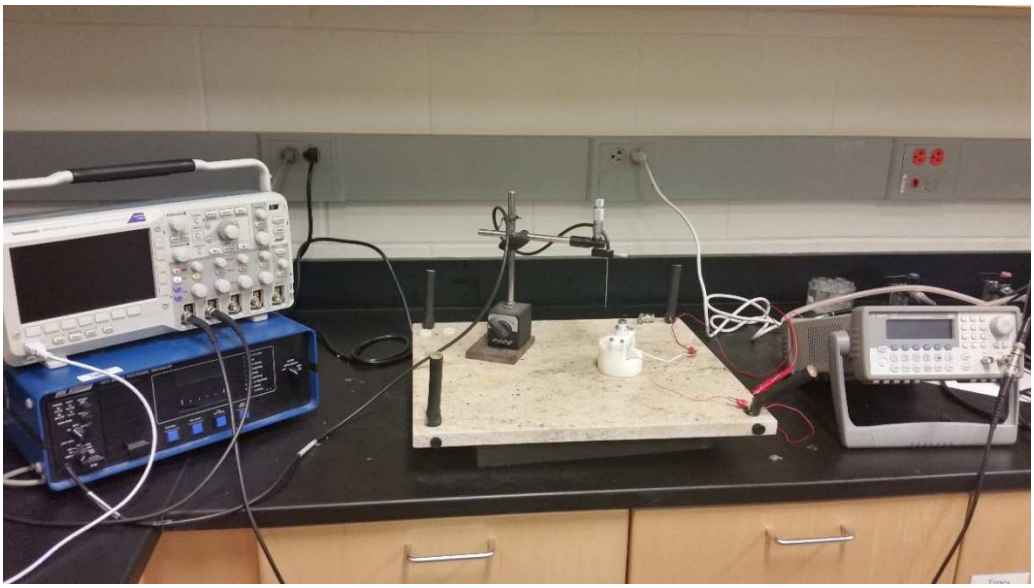


Figure 3-1: a) the setup used to measure strain (oscilloscope, function/arbitrary waveform generator, sample holder, and photonic sensor are displayed), b) the set up used to cool down and measure strain for low temperature fatigue (temperature chamber and liquid nitrogen tank displayed), and c) the set up used to heat up the ceramic for high temperature fatigue (hot plate and sample holder displayed)

b)

c)

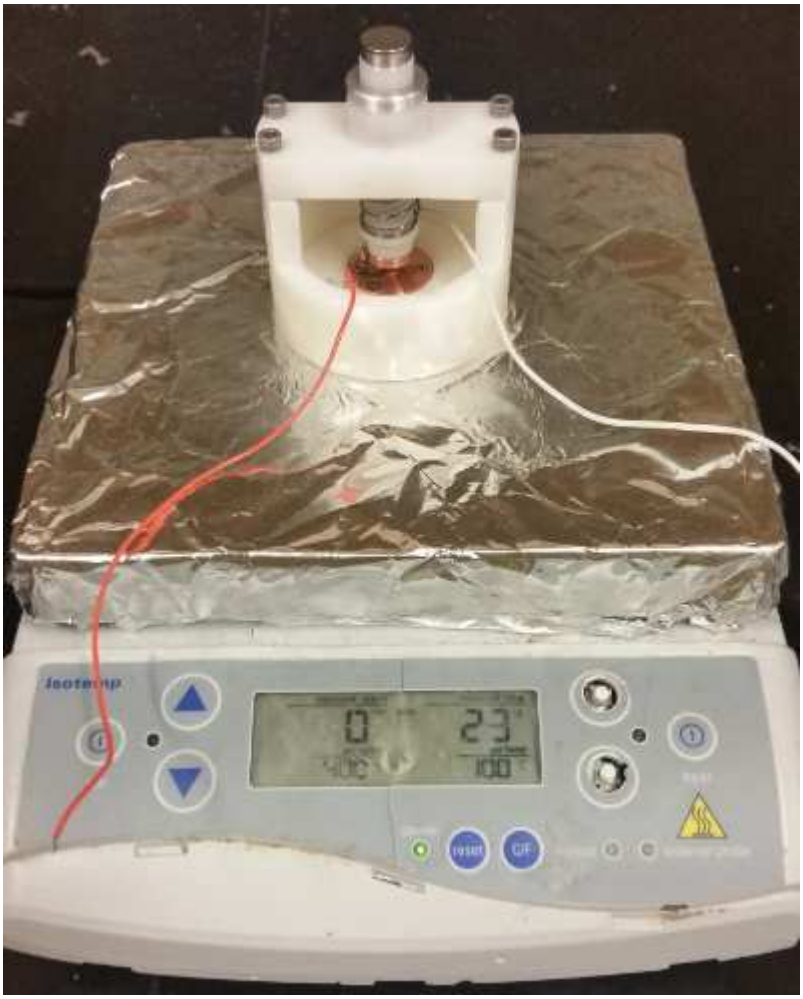


Figure 3-1 continued

The longitudinal strain was induced with an applied electric field in form of a triangular wave. The BNKT-1.5Ta pellets displayed a range of induced strain from 0.50%-0.62% at 50 kV/cm. The frequency of the wave depended on the type of experiment was being performed. All measurements used a frequency of 0.1 Hz, bipolar cycling used 4 Hz, and unipolar cycling used 25 Hz. For high-temperature experiments, the ceramic was placed in a heated silicon oil bath at the target temperature for several hours until thermal equilibrium. For low-temperature experiments, the ceramic was placed in a temperature chamber and cooled down to the target temperature with liquid nitrogen. All cycling and measurements were held at the indicated target temperature, and all samples were cycled until mechanical failure.

The temperature-dependent dielectric constant and loss tangent were measured at frequencies of 1 kHz, 10 kHz, 100 kHz, and 1 MHz at a heating rate of 4°C/min using an LCR meter (HP-4284 A, Hewlett-Packard). Crystal Structure and phase purity of BNKT-1.5Ta was analyzed by X-ray diffraction using Model D500, Siemens, Munich, Germany. Optical microscopy was used to examine fatigue cracking (OLYMPUS DP21 and SZX12). Scanning electron microscopy was implemented to examine the grain morphology of as-sintered ceramics (FEI, 1024253, 2nd Edition). Density measurements were made using the Archimedes method. Two samples were used for d_{33} measurements. They were first annealed at 350°C for 15 minutes, then poled at 50 kV/cm for 5 minutes at room temperature, and the d_{33} measurements were taken one hour and twenty-four hours after poling at room temperature. Piezoelectric coefficient d_{33} measurements were made using a Model ZJ-4B d_{33}-meter.

3.3 Results

X-ray diffraction (Figure 3-2) indicates a pseudo cubic, perovskite structure with no impurity phases. $Bi_{1/2}(Na_{0.8}K_{0.2})_{1/2}TiO_3$ is at the Morphotropic phase boundary of the rhombohedral and tetragonal phases.[41] The twin peaks around $2\theta = 46°$ might be due to {200} peak splitting, and this would be a result of tetragonal distortion of the perovskite structure.[17] Comparing the x-ray diffraction patterns of an annealed and fatigued samples show essentially no new peaks nor loss of peaks. This suggests that fatigue does not cause any permanent phase transition.

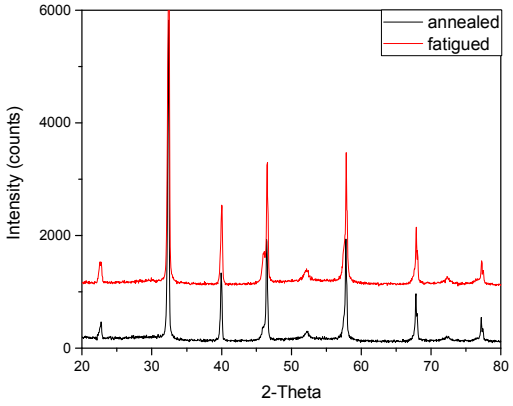


Figure 3-2: XRD pattern of BNKT-1.5Ta (a) annealed and (b) cycled for 1000 cycles. The intensity of the fatigued XRD pattern has been arbitrarily adjusted for easier comparison between the two patterns.

The grain morphology of as-sintered ceramics can be seen in Figure 3-3. The average grain size seem to match with the reported grain size of 1.25 ± 0.09 μm.[17] Figure 3-4 shows the images of the surface conditions of a fatigued sample. The discolored areas are the cracks that have formed most likely due to the formation of microcracks

during cycling. Using Archimedes method, the relative density has been measured to be 93%. Two samples were used to test how poling affected the d_{33} value. One hour after poling, the samples had d_{33} values of 18 and 20 pC/N, respectively, and twenty-four hours after poling, the samples had d_{33} values of 10 and 11 pC/N, respectively. This suggest BNT-1.5Ta does not stay polarized easily, and this match up with theories that relaxors do not stay poled because of nano-domains.

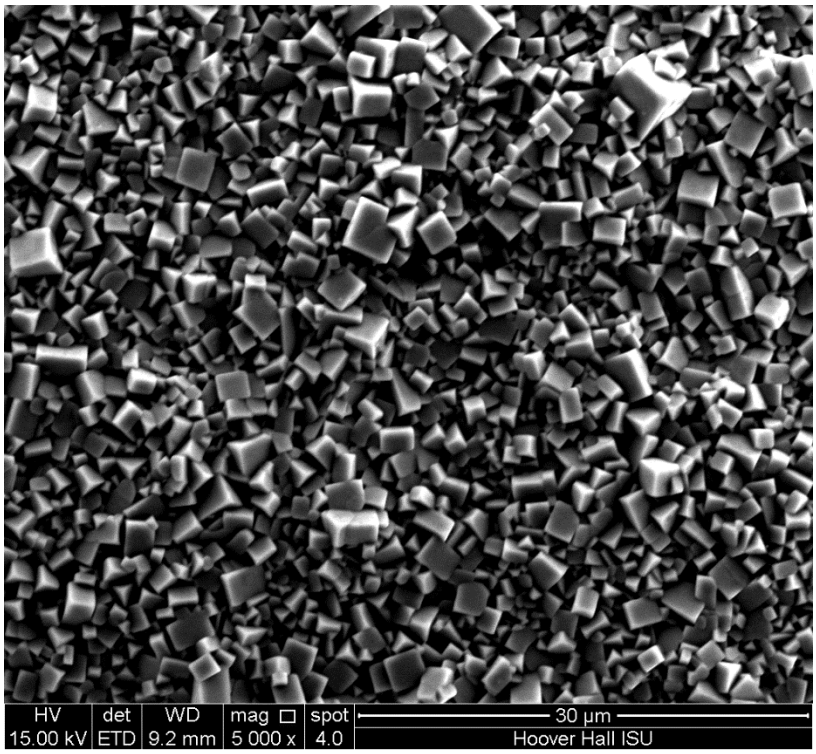


Figure 3-3: SEM image of as-sintered BNKT-1.5Ta surface

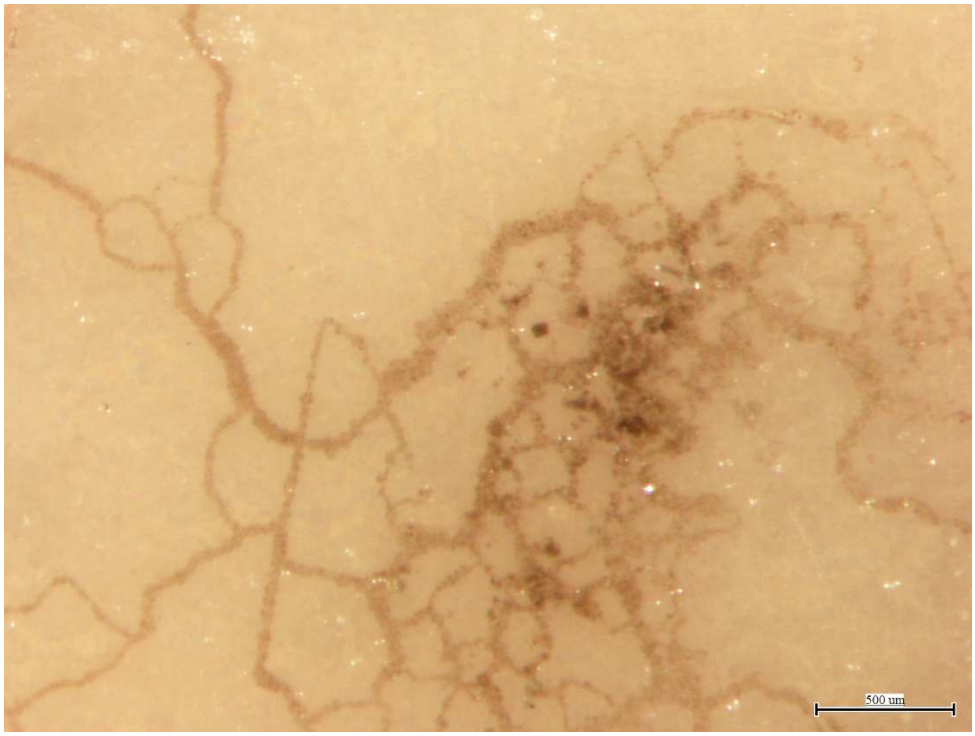
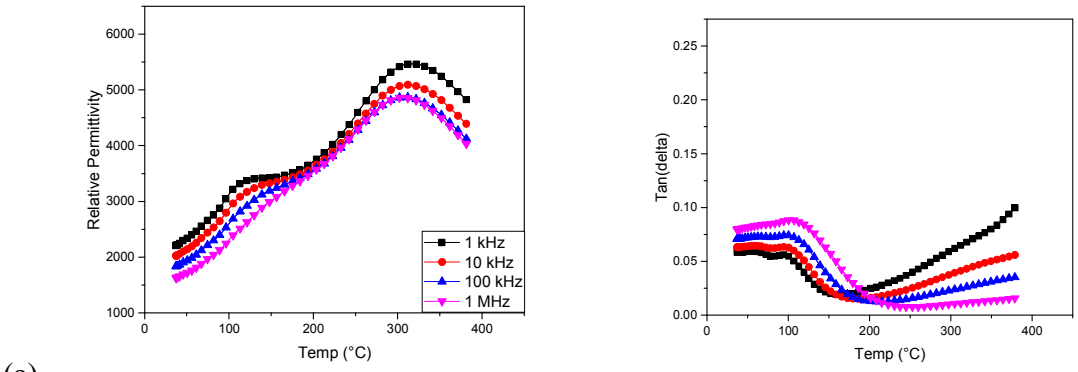
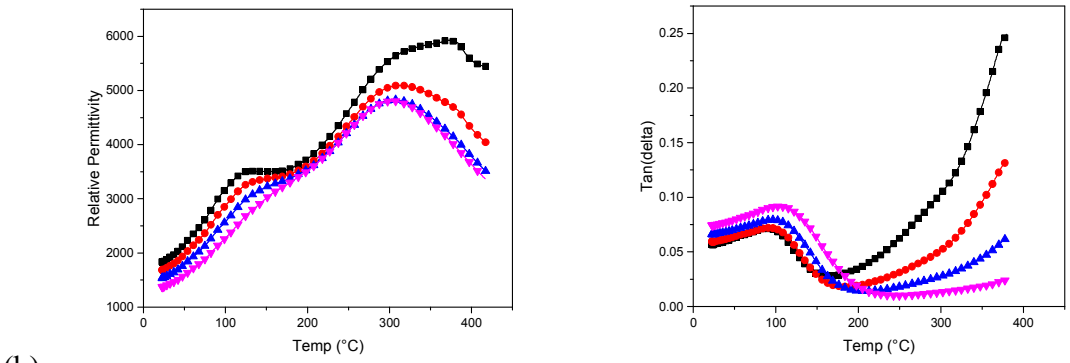


Figure 3-4: Optical image of surface of fatigued BNKT-1.5Ta sample

Figure 3-5 show the dielectric constant and loss tangent for the same sample annealed and cycled for 1000 cycles at 4 Hz under an applied electric field of 50 kV/cm. It is clear from the data that BNT-1.5Ta has frequency dispersion and this suggests a relaxor phase.[17] Though the BNT-1.5Ta sample follows similar behavior after annealing and after 1000 cycles, especially with respect to frequency dispersion, there are a few key differences. Past 300°C, where the permittivity would peak around 320-325°C as seen in literature and the annealed state, the 1 kHz and 10 kHz frequencies of the 1000 cycle dielectric graph show unusual high-temperature behavior and T_{max} of 390°C and 330°C, respectively. In addition, the 1000 cycle case has higher dielectric loss. A possible reason for the stranger, and higher dielectric behavior at higher temperatures could be due to crack formation and domain pinning. This would certainly cause higher dielectric loss. The uncertainty in relative permittivity roughly 10-30.



(a)



(b)

Figure 3-5: Dielectric measurements of BNKT-1.5Ta sample after (a) annealing and (b) 1000 cycles

Figures 3-6, 3-7, and 3-8 shows the bipolar and unipolar strain and polarization data as a function of number of cycles at room temperature (25°C), 65°C, and 4°C, respectively. The temperature affects the strain and polarization hysteresis. The low temperature fatigue occurs below the depolarization temperature of BNKT-1.5Ta, and this can change the perovskite structure to a ferroelectric phase compared to an ergodic relaxor phase at room and high temperature. This can be visually seen in the bipolar strain graphs as a "butterfly" shape (ferroelectric) compared to a "sprout" shape (relaxor), and in the bipolar polarization graphs, a round hysteresis (ferroelectric) compared to a

"pinched" hysteresis (relaxor). Another difference can be seen in the bipolar polarization graphs. For the low temperature, the bipolar polarization graph shows relatively good fatigue resistance while the room temperature and high-temperature bipolar polarization graphs show an extreme decrease in polarization starting at 10^5 and 10^3 cycles, respectively. This suggests the relaxor phase undergoes a critical threshold for electric fatigue before reaching a critical threshold for mechanical fatigue while in the ferroelectric phase the piezoceramics undergoes electrical and mechanical fatigue at the similar rates and is more fatigue resistant.

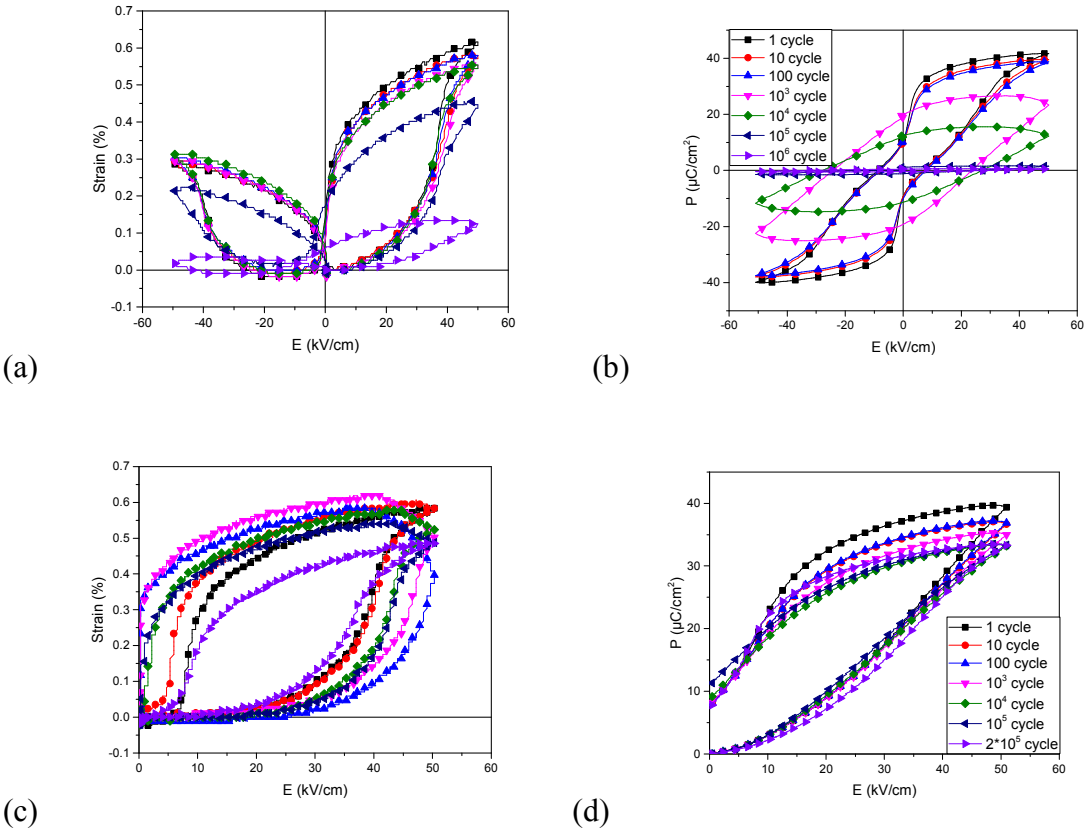


Figure 3-6: Room temperature (25°C) fatigue: (a) bipolar strain, (b) bipolar polarization, (c) unipolar strain, (d) unipolar polarization

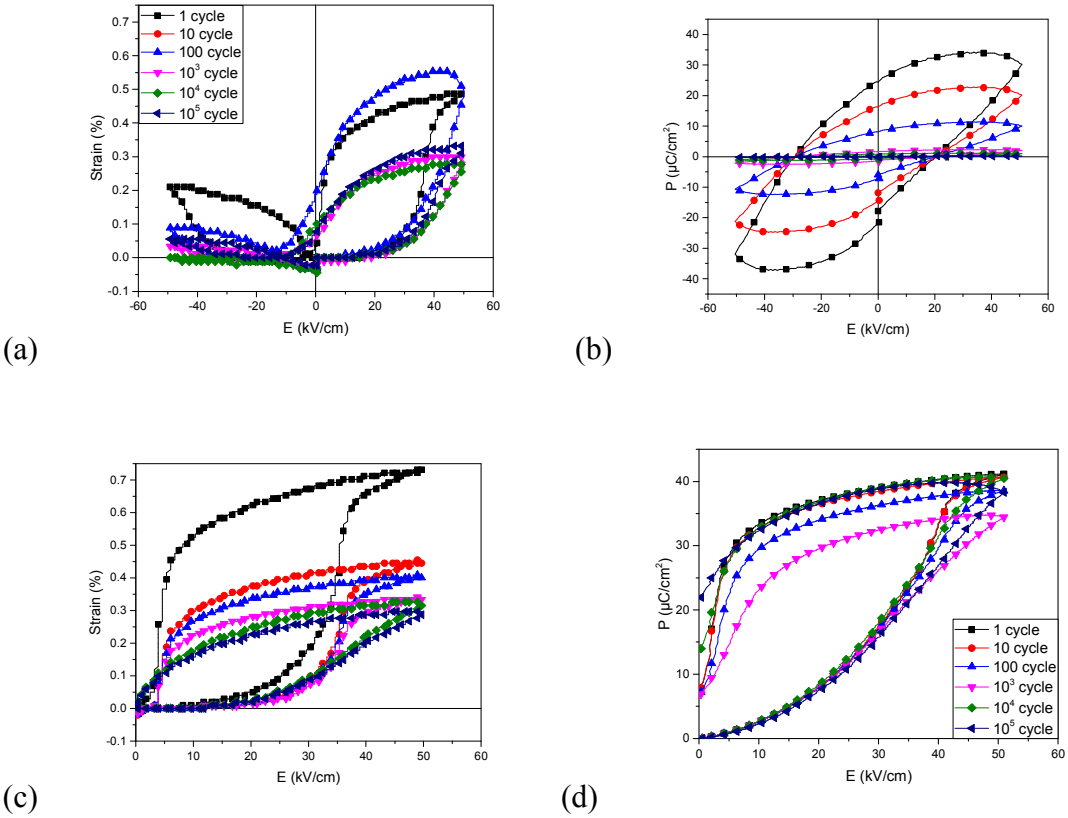


Figure 3-7: High temperature (65°C) fatigue: (a) bipolar strain, (b) bipolar polarization, (c) unipolar strain, (d) unipolar polarization

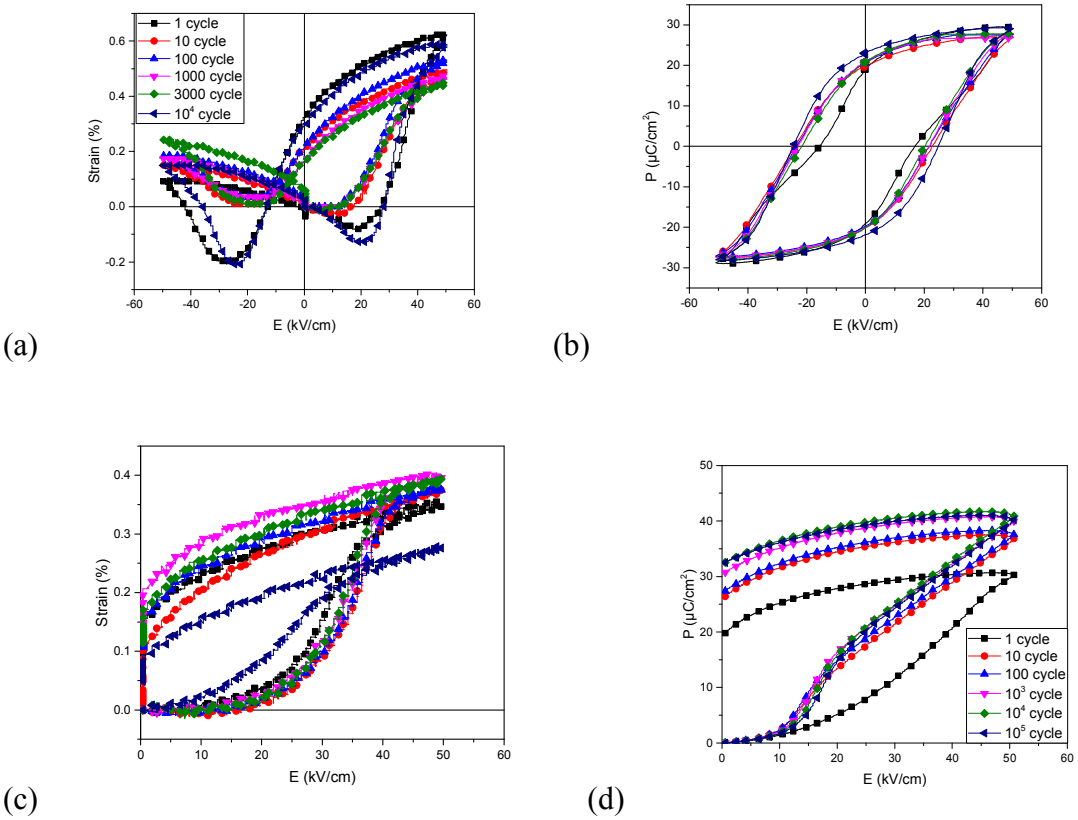


Figure 3-8: Low temperature (4°C) fatigue: (a) bipolar strain, (b) bipolar polarization, (c) unipolar strain, (d) unipolar polarization

A common trait regardless of temperature and type of cycling is that fatigue tends to decrease the max strain and max polarization as a function of number of cycles as seen in Figure 3-9.

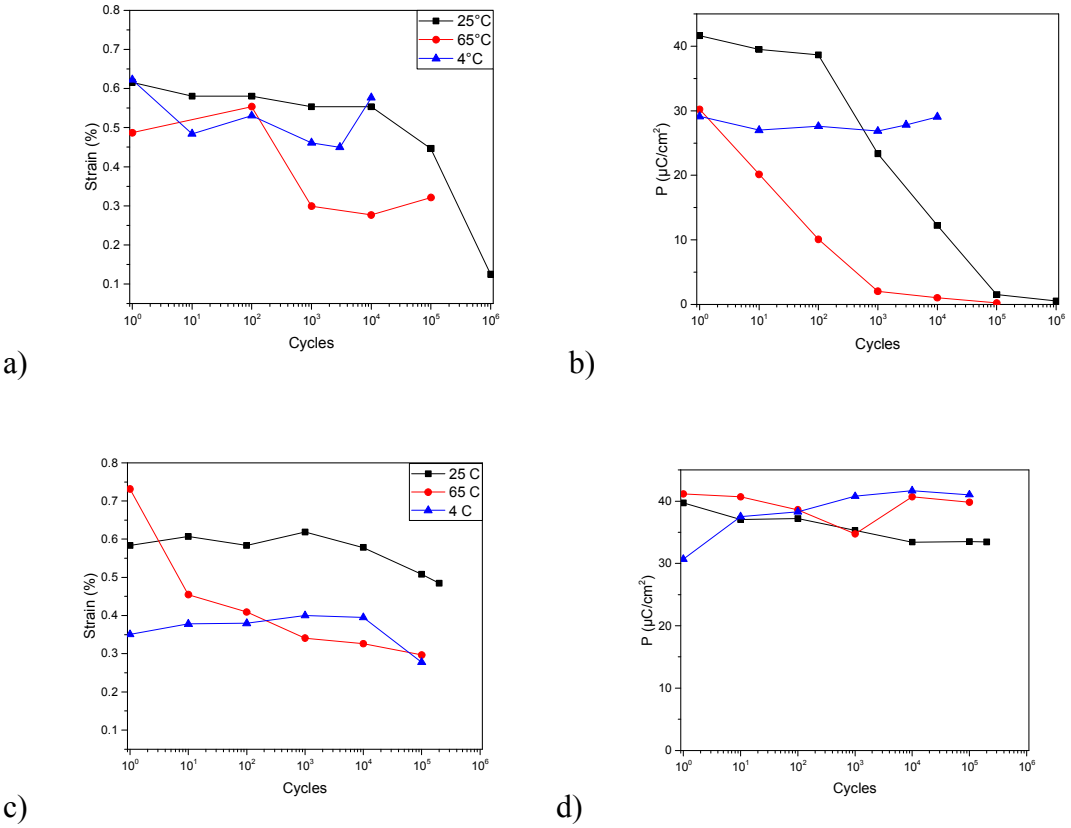


Figure 3-9: The (a) maximum strain in bipolar fatigue, (b) maximum polarization in bipolar fatigue, (c) maximum strain in unipolar fatigue, and (d) maximum polarization in unipolar fatigue as a function of number of cycles with respect to temperature. The data was extracted from the data presented in Figures 3-6, 3-7, and 3-8.

Though strain or polarization may seem to increase in value at one point or another, in general, strain and polarization will decrease. The amount or percentage a strain or polarization depends on temperature and type of cycling. Generally, unipolar fatigue tends to more fatigue resistant than bipolar fatigue as seen by the fact there is only 10% loss in polarization and 18% loss in strain after 10^5 cycles in 25°C unipolar fatigue compared to 90% loss in polarization after 10^5 cycles and 75% loss in strain after 10^6 cycles in 25°C bipolar fatigue. An explanation for this is that there is no electric field

reversal in unipolar fatigue, and as a result, there is no polarization reversal. In addition, one bipolar cycle is equivalent to two unipolar cycles, which means a sample undergoing bipolar fatigue would degrade twice as fast as a sample undergoing unipolar fatigue. In the bipolar fatigue graphs, the samples tend to show asymmetric hysteresis which is due to internal bias from charged point defects.[17] The hysteresis may become less asymmetrical with increasing cycle number, and this is a sign that degradation mechanisms are beginning to have an effect on the domains or grains of the samples. Another observation seen in all the polarization and strain graphs regardless of type or cycling or temperature is a general round of hysteresis. This is most likely due to the fact that either domains are responding more slowly to a reversal in electric field or some domains are pinned in certain orientations.

A noteworthy observation is that there is a wide range of maximum strain different pellets can demonstrate. A possible explanation for this range of values is sample-to-sample variation among pellets due to factors in the solid synthesis process. This includes the addition of binder, pressing the green pellets, and pores and other defects that form due to the loss of binder during sintering and impurities inherent from reagent powders with less than 100% purity.

3.4 Conclusion

BNKT-1.5Ta shows properties similar to those that have been reported in the literature.[17] This solid solution can undergo some severe degradation: strain can be reduced by 50% after 10^4 cycles and 75% after 10^6 cycles while polarization can be reduced up to 90% after as little as 10^5 cycles in some cases. This suggest that BNKT-1.5Ta may not be suitable for applications that need a consistently highly effective piezoelectric material, but may work for applications that would only require few cycles of operation. The large electrostrain may be good for applications that need a large displacement.[17] Further modification of BNKT-1.5Ta solid solution is needed to find a composition that has better fatigue resistance.

3.5 Acknowledgments

This work was funded by the National Science Foundation (NSF) through Grant DMR-1465254.

CHAPTER 4: CONCLUSION

4.1 General Conclusions

This thesis was designed to give the reader a brief introduction of piezoceramics, and more information can be obtained through the articles and books referenced. The research presented in chapter 3 is part of a larger investigation of BNKT-1.5Ta properties. The main focus of the research was the fatigue properties of BNKT-1.5Ta. Although it has a large initial electrostrain, BNKT-1.5Ta generally does not have good fatigue resistance beyond 10^4 cycles. The low fatigue resistance may be related to the high electrostrain due to the fact that high strain are more likely to cause cracks and that both properties may be the result of inherent defects in the ceramic. Further investigation of the microstructure is needed to truly understand the degradation effects of BNKT-1.5Ta.

4.2 Suggestions for Future Research

The mechanisms of lead-free piezoceramics fatigue still needs further research. Two topics to look into are what are the specific mechanisms that cause electric fatigue and how electric and mechanical degradation mechanisms affect each other. This can be done by looking at the phase morphology and crystal structure using TEM. The use of TEM allows one to identify the grains and domains in a ceramic, and this may provide an opportunity to witness the degradation mechanisms directly. Another study could be to study the fatigue properties of piezoceramics with cycling as a function of mechanical

loading. This is useful for applications such as for sensor that use applied stress such as scales and pressure plates. This could be used as an opportunity to see if degradation mechanisms of the direct and converse piezoelectric effect in lead-free ceramics are the same or differ. Another future study could focus on how the shape of the sample affects fatigue resistance. In this thesis, the samples were essentially disks with a circular cross-section; what if the cross-section was square or some other arbitrary shape? Would it make a difference if the field was applied through small areas on opposing sides of the disk instead on the faces? Could electrical properties such as polarization of BNT-1.5Ta be recovered through annealing even if there are signs of mechanical fatigue? There are many questions yet to be answered in this field.

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